

DENSE LEAD AND BISMUTH SCINTILLATORS

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ABSTRACT

Scintillation intensities of dense lead and bismuth compounds at 300 K are reported relative to BGO. For luminous materials the Pb and Bi site asymmetry is quantified using a principal axis transform of the charge distribution and correlated with the Stokes shift of their emission. Preliminary results of *ab initio* cluster calculations of electronic structure are also presented.

INTRODUCTION

Lead and bismuth are the heaviest nonradioactive elements in the periodic table. Luminescent compounds of these elements can have short radiation lengths and large photoelectric fractions and therefore are attractive for use in detectors for calorimetry in high energy physics [1] and for medical imaging (PET).[2] In the search for new inorganic scintillators, a large number of lead and bismuth compounds have been investigated [3,4] but thus far none have exhibited a light yield superior to that of Bi₄Ge₃O₁₂ (BGO). We have extended this survey using crystal diffraction databases [5,6] to identify dense Pb- or Bi-based hosts. The results are summarized in Table 1 where compounds are grouped by scintillation light output relative to that of BGO. Samples were generally in the form of powders or polycrystalline materials. All measurements were performed at room temperature using a pulsed x-ray apparatus and detection techniques described elsewhere.[7] The scintillation spectra were not characterized. At this stage our

Table 1. Reported scintillation intensity at room temperature for lead and bismuth compounds relative to that of Bi₄Ge₃O₁₂ [from references [3,4] and from this work (*)].

10–100% BGO	1.0–10% BGO	≤ 1% BGO
Bi ₄ Ge ₃ O ₁₂ Bi ₄ Si ₃ O ₁₂ PbSO ₄ *PbHPO ₄ *PbAl ₂ O ₄	PbCO ₃ PbWO ₄ *Bi ₂ Al ₄ O ₉ *Pb ₅ (PO ₄) ₃ F PbCl ₂ *PbOHCl *PbOHBr *PbOHI	Bi ₂ O ₃ , Bi ₂ CO ₅ , BiPO ₄ , Bi ₂ (SO ₄) ₃ , BiBO ₃ , Bi(OH) ₃ , BiF ₃ , BiCl ₃ , BiBr ₃ , BiOCl, BiOBr, *BiKF ₄ , *BiK ₄ F ₇ , *Bi ₃ KF ₁₀ , *Bi ₄ KF ₁₃ , *BiHfF ₇ , *BiNa ₄ I ₇ , *Bi ₂ Cs ₃ Br ₉ , *Bi ₂ BaF ₈ , Bi ₁₂ GeO ₂₀ , Bi ₁₂ SiO ₂₀ , Bi ₄ Ti ₃ O ₁₂ , Bi ₂ Ti ₂ O ₇ , Bi ₂ WO ₆ , Bi ₂ W ₂ O ₉ , Bi ₂ W ₃ O ₁₂ , Bi ₂ Na(WO ₄) ₂ , BiNO ₄ , Bi(MoO ₄) ₃ , *Bi ₂ Sn ₂ O ₇ , Bi ₂ Sn ₃ O ₉ , Bi(C ₂ H ₃ O ₂) ₃ , Bi ₁₂ PbO ₂₀ , BiPbFO ₂ , PbF ₂ , PbCl ₂ , PbBr ₂ , PbI ₂ , Pb(NbO ₃) ₂ , PbSO ₃ , PbC ₂ O ₄ , Pb(OH) ₂ , Pb(VO ₃) ₂ , PbB ₃ O ₇ , PbZrO ₃ , Pb ₂ SiO ₄ , Pb(NO ₃) ₂ , PbSeO ₄ , PbSiO ₃ , PbTiO ₃ , *PbHfO ₃ , PbTa ₂ O ₆ , PbMoO ₄ , Pb ₂ P ₂ O ₇ , Pb ₃ P ₂ O ₈ , Pb(NbO ₃) ₂ , Pb(ClO ₄) ₂ •H ₂ O

intent is to survey and screen those materials operating at room temperature that warrant further spectroscopic studies and growth efforts.

Although the luminescence properties of various Pb- and Bi-doped materials and lead and bismuth compounds have been investigated for many decades and most of the spectroscopic features are generally understood [8], our ability to predict efficient room-temperature Pb or Bi luminescence is still limited and new features continue to be reported (see, for example, [9]). The number of Bi and Pb compounds exhibiting intense photo- or x-ray-excited luminescence at 300 K is small. The structure and spectroscopic properties of several of these compounds are given in Table 2. ($T_{1/2}$ is the temperature at which the luminescence is reduced to one-half of its low temperature value.) Of the bismuth oxide–germanium oxide system, only the compounds with large germania content exhibit luminescence. Similar behavior is observed for the Bi_2O_3 – SiO_2 system. The 1:2 compounds of the bismuth aluminate and gallate systems and the 1:1 compounds of the lead aluminate and gallate systems exhibit intense luminescence at room temperature.[10] Although their densities are not high, there are other compositions, particularly the 2:1 compound $\text{Bi}_4\text{Al}_2\text{O}_9$, that warrant investigation. Many different lead phosphate compositions exist with a wide range of densities. The 3:1 compound in Table 2 is moderately dense but has a quenching temperature of only 150 K; no significant luminescence was detected for several other lead phosphates down to liquid helium temperatures.[11]

Table 2. Structure and spectroscopic properties of lead and bismuth compounds.[10-15]

Compound	Density (g/cm ³)	Oxygen CN: (distances – Å)	Stokes shift (eV)	Quench $T_{1/2}$ (K)
<u>Bismuth:</u>				
$\text{Bi}_{12}\text{GeO}_{20}$ (6:1) (<i>cubic</i>)	9.2	7: 2.07–3.19	1.0/1.5	25/140
$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (2:3) (<i>cubic</i>)	7.1	6: 2.16–2.62	2.25	270
$\text{Bi}_2\text{Ge}_3\text{O}_9$ (1:3) (<i>hexagonal</i>)	6.2	6: 2.14–2.75	2.5	120
$\text{Bi}_3\text{B}_5\text{O}_{12}$ (3:5) (<i>orthorhombic</i>)	6.2	6: 2.12–2.68	2.1	150
$\text{Bi}_2\text{Al}_4\text{O}_9$ (1:2) (<i>orthorhombic</i>)	6.2	6: 2.24–2.78	2.2	280
<u>Lead:</u>				
PbAl_2O_4 (1:1) (<i>monoclinic</i>)	5.5	6: 2.27–3.27	2.4	>300
PbGa_2O_4 (1:1) (<i>monoclinic</i>)	6.6	6: 2.28–3.30	2.6	290
PbSO_4 (<i>orthorhombic</i>)	6.4	8: 2.63–2.93	2.2	>300
PbHPO_4 (<i>monoclinic</i>)	5.6	6: 2.35–2.87	2.9	220
$\text{Pb}_3(\text{PO}_4)_2$ (3:1) (<i>monoclinic</i>)	7.5	8: 2.54–2.97	1.5	150

SITE ASYMMETRY

Blasse and co-workers have noted that luminous Pb and Bi compounds generally have Pb or Bi ions with asymmetric coordination polyhedra. For such off-center sites, large displacive relaxation may occur in the excited electronic state resulting in large Stokes shifts. We have quantified the asymmetry by forming a matrix of the coordinates and charges of the surrounding ions. The program SEXIE [16] was used to identify the coordination shells. Note that even when there is no symmetry of the surrounding ligands, it is still possible to define a principal axis system.[17] Using a simple point charge for the ligands, the coordination matrix is diagonalized using a Jacobi transformation, thus yielding a set of three

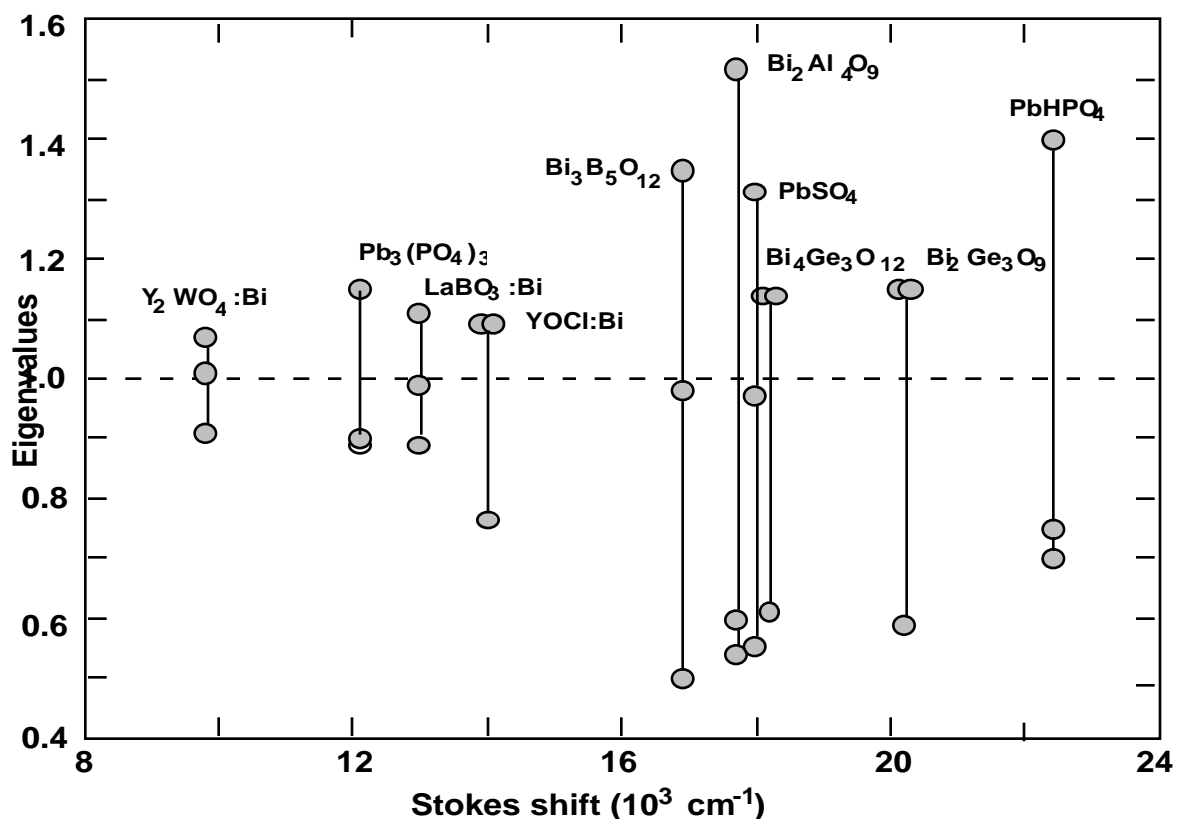


Figure 1. Eigenvalues of a principal axis transformation of the nearest neighbor charge distribution for Pb and Bi materials as a function of the Stokes shift of their luminescence

eigenvalues (renormalized to 1 for a spherical charge distribution) which are the semi-axes of the charge ellipsoid. The results for several Pb and Bi compounds are shown in Fig.1. Large Stokes shifts correlate with large distortions of the charge distribution. What is needed is guidance in predicting the quenching temperature. As can be seen from Table 2, there is not a clear correlation between charge asymmetry, Stokes shift, and quenching temperature.

CLUSTER CALCULATIONS

We have begun using *ab initio* calculations of ion clusters to simulate the electronic structure of BGO and BSO crystals. (In an early investigation of BGO, a $(\text{BiO}_6)^{9-}$ cluster was treated using molecular orbital theory.[18]) We have tried several different clusters and embedding approaches. To date the most meaningful results have been obtained with a cluster consisting of a Bi ion surrounded by six O and three Ge. The cluster was saturated with fifteen H atoms. The total number of valence electrons was 80. All computations were performed using gaussian bases and Hay-Wadt pseudopotentials which include relativistic effects necessary for heavier atoms. We first optimized the cluster configuration for the ground state minimizing the total self-consistent-field (SCF) energy. The final ground state configuration is very close to that of the known crystal structure. Excited states are treated using a singles configuration interaction calculation. We re-optimized the cluster geometry for the excited triplet state to obtain the emission energy and Stokes shift. In the lowest excited state the Bi moves slightly towards the center of the cluster, but one of the nearest neighbor oxygens binding the Bi with a Ge moves an unexpectedly large 1.1 Å away from the Bi. (This behavior was confirmed from calculations of bismuth trihalide molecules.) A large Stokes shift is predicted but is larger

than observed because the absorption energies are about 20% larger than the experimental values and the emission energies are 10% lower. We also estimated the lifetime of the lowest excited state using a spin-orbit term to mix singlet and triplet. The calculated lifetime of BGO is about five times longer than that of BSO. Experimentally it is found to be three times longer. The computed Mulliken atomic charge on Bi for the triplet state is close to 1.5 instead of the formal charge of +3. This partially covalent binding between Bi and the three closest oxygens implies an approximate C_{3v} symmetry, thus the 3P state of Bi^{3+} is split into two electronic states. At the same time, the spin population is almost evenly split between the Bi and the displaced oxygen. In this case a molecular orbital picture of the excitation is more appropriate. These results are in contrast to those obtained for other $6s^2$ ion scintillators, such as NaI:Tl, where the thallium was found to behave almost as a Tl^+ ion.[19]

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Bi ₄ Si ₃ O ₁₂	PbWO ₄	BiF ₃ , BiCl ₃ , BiBr ₃ , BiOCl, BiOBr, *BiKF ₄ , *BiK ₄ F ₇ ,
PbSO ₄	*Bi ₂ Al ₄ O ₉	*Bi ₃ KF ₁₀ , *Bi ₄ KF ₁₃ , *BiHfF ₇ , *BiNa ₄ I ₇ , *Bi ₂ Cs ₃ Br ₉ ,
*PbHPO ₄	*Pb ₅ (PO ₄) ₃ F	*Bi ₂ BaF ₈ , Bi ₁₂ GeO ₂₀ , Bi ₁₂ SiO ₂₀ , Bi ₄ Ti ₃ O ₁₂ , Bi ₂ Ti ₂ O ₇ ,
*PbAl ₂ O ₄	PbCl ₂	Bi ₂ WO ₆ , Bi ₂ W ₂ O ₉ , Bi ₂ W ₃ O ₁₂ , Bi ₂ Na(WO ₄) ₂ , BiNO ₄ ,
	*PbOHCl	Bi(MoO ₄) ₃ , *Bi ₂ Sn ₂ O ₇ , Bi ₂ Sn ₃ O ₉ , Bi(C ₂ H ₃ O ₂) ₃ ,
	*PbOHBr	Bi ₁₂ PbO ₂₀ , BiPbFO ₂ , PbF ₂ , PbCl ₂ , PbBr ₂ , PbI ₂ ,
	*PbOHI	Pb(NbO ₃) ₂ , PbSO ₃ , PbC ₂ O ₄ , Pb(OH) ₂ , Pb(VO ₃) ₂ ,
		PbB ₃ O ₇ , PbZrO ₃ , Pb ₂ SiO ₄ , Pb(NO ₃) ₂ , PbSeO ₄ ,
		PbSiO ₃ , PbTiO ₃ , *PbHfO ₃ , PbTa ₂ O ₆ , PbMoO ₄ ,

		$\text{Pb}_2\text{P}_2\text{O}_7$, $\text{Pb}_3\text{P}_2\text{O}_8$, $\text{Pb}(\text{NbO}_3)_2$, $\text{Pb}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
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